

**PROCESS FOR THE MANUFACTURE OF MULTI-PLY TISSUE**

THOMAS HÖRNER  
SCOTT J. LOUGHRAN  
MARIANNE MALMBAK  
ANJA WERTH

**CROSS REFERENCE TO RELATED APPLICATION**

This application is a divisional of copending U.S. Application No. 09/831,784 filed May 14, 2001.

**FIELD OF INVENTION**

The present invention relates to multi-ply tissue, and in particular to facial tissue, and disposable handkerchiefs.

Paper webs or sheets, sometimes called tissue or paper tissue webs or sheets, find extensive use in modern society. Such items as facial and toilet tissues are staple items of commerce. It has long been recognised that four important physical attributes of these products are their strength, their softness, their absorbency, including their absorbency for aqueous systems; and their lint resistance. Research and development efforts have been directed to the improvement of each of these attributes without seriously affecting the others as well as to the improvement of two or three attributes simultaneously.

Softness is the tactile sensation perceived by the consumer as he/she holds a particular product, rubs it across his/her skin, or crumples it within his/her hand. This tactile sensation is a combination of several physical properties. One of the more important physical properties related to the softness is generally considered by those skilled in the art to be the stiffness of the paper tissue from which the product is made. Stiffness, in turn, is usually considered to be directly dependent on the dry tensile strength of the web.

Strength is the ability of the product to maintain physical integrity and to resist tearing, bursting, and shredding under use conditions.

Absorbency is the measure of the ability of a product to absorb quantities of liquid, particularly aqueous solutions or dispersions. Overall absorbency as perceived by the human consumer is generally considered to be a combination of the total quantity of a liquid a given mass of tissue paper will absorb at saturation as well as the rate at which the mass absorbs the liquid.

Lint resistance is the ability of the fibrous product, and its constituent webs, to bind together under use conditions, including when wet. In other words, the higher the lint resistance is, the lower the propensity of the web to lint will be.

WO95/11343, published on 27<sup>th</sup> April 1995, discloses a process for making layered paper tissues. Example 3 discloses a two-ply facial tissue having a basis weight of about 32 g/m<sup>2</sup> (20 lbs/3000 sq. ft.) The tissue of this example comprises 0.475% of a wet strength resin.

US-A-4 481 243, issued on 6<sup>th</sup> November 1984 discloses facial tissues which comprise multiple plies secured together by embossing only along the margins of the tissue.

Disposable paper products having high wet burst strength are known, for example Bounty™, sold by The Procter & Gamble Company, has a wet burst strength which is greater than 200 g. However such kitchen towels are embossed over the whole surface which results in a surface texture which is rough and does not provide a suitably smooth wiping surface for blowing the nose.

Facial tissues are commercially available comprising at least two plies, the tissue having a surface area in one plane, and a thickness orthogonal to the plane, wherein the thickness is a caliper of at least 0.35mm, and wherein the tissue has an unembossed wiping surface over a major part of the surface area of the tissue. However the rather low wet burst strength of today's facial tissues often results in tearing or bursting which in turn results in contamination of the user's hand with mucus or other bodily fluids.

The object of the present invention is to provide a multi-ply facial tissue having the at least the desired softness and absorbency of known facial tissues, but also providing enhanced protection against tearing or bursting when used, in particular when used for blowing the nose.

### Summary of the Invention

The invention relates to a process for the manufacture of the multi-ply tissue, wherein the process comprises the steps of :

- 5       - mechanically refining a first slurry of fibers wherein the fibers have an average length of at least 2mm, preferably the first slurry comprises a substantial proportion of softwood fibers, such as Nothern Softwood Kraft fibers;
- mixing the refined slurry with a second slurry of fibers, the average length of the fibers of the second slurry being shorter than the average length of the fibers of the first slurry, preferably the second slurry comprises a substantial proportion of  
10       hardwood fibers, such as eucalyptus fibers;
- providing a embryonic web upon a foraminous surface, the composition of fibers in the embryonic web being substantially homogeneous throughout the thickness of the web;
- 15       - removing water from the embryonic web to form a ply; and
- juxtaposing at least two plies to form the multi-ply tissue.

Most preferably, the ratio of long softwood fibers to shorter hardwood fibers is greater than 60:40, and preferably about 70:30.

20

### Detailed Description of the Invention

The present invention may contain, as a highly preferred component, up to about 3.0%, preferably at least 0.5%, and more preferably at least 0.8% by weight, on a dry fiber weight basis, of wet strength chemical agent, such as water-soluble permanent and temporary wet strength resin.

25

Wet strength resins useful herein can be of several types. For example, Westfelt described a number of such materials and discussed their chemistry in Cellulose Chemistry and Technology, Volume 13, at pages 813-825 (1979).

30

Usually, the wet strength resins are water-soluble, cationic materials. That is to say, the resins are water-soluble at the time they are added to the papermaking furnish. It is quite possible, and even to be expected, that subsequent events such as cross-linking will render the resins insoluble in water. Further some resins are soluble only under specific conditions, such as

over a limited pH range. Wet strength resins are generally believed to undergo a cross-linking or other curing reactions after they have been deposited on, within, or among the papermaking fibers. Cross-linking or curing does not normally occur so long as substantial amounts of water are present.

5

Of particular utility are the various polyamide-epichlorohydrin resins. These materials are low molecular weight polymers provided with reactive functional groups such as amino, epoxy, and azetidinium groups. The patent literature is replete with descriptions of processes for making such materials, including US-A-3 700 623, issued to Keim on October 24<sup>th</sup> 1972, and US-A-3 772 076, issued to Keim on November 13<sup>th</sup> 1973.

10

Polyamide-epihydrochlorin resins sold under the trademarks Kymene 557H and Kymene LX by Hercules Inc. of Wilmington, Delaware, are particularly useful in this invention. These resins are generally described in the aforementioned patents to Keim.

15

Base-activated polyamide-epichlorohydrin resins useful in the present invention are sold under the Santo Res trademark, such as Santo Re 31, by Monsanto Company of St. Louis, Missouri. These types of materials are generally described in US-A-3 855 158 issued to Petrovich on December 17<sup>th</sup> 1974; US-A-3 899 388 issued to Petrovich on August 12<sup>th</sup> 1975; US-A-4 129 528 issued to Petrovich on December 12 1978; US-A-4 147 586 issued to Petrovich on April 3<sup>rd</sup> 1979; and US-A-4 222 921 issued to Van Eenam on September 16<sup>th</sup> 1980.

20

Other water-soluble cationic resins useful hererin are the polyacrylamide resins such as those sold under the Parex trademark, such as Parex 631NC, by American Cyanamid Company of Sandford, Connecticut. These materials are generally described in US-A-3 556 932 issued to Coscia et al on January 19<sup>th</sup> 1971; and US-A3 556 933 issued to Williams et al on January 19<sup>th</sup> 1971.

25

Other types of water-soluble resins useful in the present invention include acrylic emulsions and anionic styrene-butadiene latexes. Numerous examples of these types of resins are provided in US-A3 844 880. Meisel Jr et al, issued October 29<sup>th</sup> 1974. Still other water-soluble cationic resins finding utility in this invention are the urea formaldehyde and melamine formaldehyde resins. These polyfunctional, reactive polymers have molecular weights on the

30

order of a few thousand. The more common functional groups include nitrogen containing groups such as amino groups and methylol groups attached to the nitrogen. Although less preferred, polyethylenimine type resins find utility in the present invention.

- 5           More complete descriptions of the aforementioned water-soluble resins, including their manufacture, can be found in TAPPI Monograph Series No. 29, "Wet Strength in paper and Paperboard, Technical Association of the Pulp and Paper Industry (New York; 1965).

- Temporary wet strength agents, such as modified starch may also, optionally, be used.
- 10   Combinations  
          of permanent and temporary wet strength agents may be used.

- The present invention may contain dry strength chemical agents, preferably at levels up to 3% by weight, more preferably at least 0.1% by weight, on a dry fiber weight basis. A highly
- 15   preferred dry strength chemical agent is carboxymethyl cellulose. Other suitable dry strength chemical agents include polyacrylamide (such as combinations of Cypro™ 514 and Accostrength™ 711 produced by American Cyanamid of Wayne, N.J.); starch (such as corn starch or potato starch); polyvinyl alcohol (such as Airvol™ 540 produced by Air Products Inc. of Allentown, PA); guar or locust bean gums; and polyacrylate latexes. Suitable starch materials
- 20   may also include modified cationic starches such as those modified to have nitrogen containing groups such as amino groups and methylol groups attached to nitrogen, available from National Starch and Chemical Company (Bridgewater, NJ).

- Chemical softening compositions, comprising chemical debonding agents are optional
- 25   components of the present invention. US-A-3 821 068, issued June 28<sup>th</sup>, 1974 teaches that chemical debonding agents can be used to reduce the stiffness, and thus enhance the softness, of a tissue paper web. US-A-3 554 862, issued on January 12<sup>th</sup> 1971 discloses suitable chemical debonding agents. These chemical debonding agents include quaternary ammonium salts.

- 30           Preferred chemical softening compositions comprise from about 0.01% to about 3.0% of a quaternary ammonium compound, preferably a biodegradable quaternary ammonium compound; and from about 0.01% to about 3.0% of a polyhydroxy compound; preferably selected from the group consisting of glycerol, sorbitols, polyglycerols having an average

molecular weight of from about 150 to about 800 and polyoxyethylene glycols and polyoxypropylene glycols having a weight average molecular weight from about 200 to 4000. Preferably the weight ratio of the quaternary ammonium compound to the polyhydroxy compound ranges from about 1.0:0.1 to 0.1:1.0. It has been discovered that the chemical softening composition is more effective when the polyhydroxy compound and the quaternary ammonium compound are first premixed together, preferably at a temperature of at least 40°C, before being added to the papermaking furnish. Either additionally, or alternatively, chemical softening compositions may be applied to the substantially dry tissue paper web, for example by means of a printing process (N.B. all percentages herein are by weight of dry fibers, unless otherwise specified).

Examples of quaternary ammonium compounds suitable for use in the present invention include either unmodified, or mono- or di- ester variations of : well-known dialkyldimethylammonium salts and alkyltrimethyl ammonium salts. Examples include the di-ester variations of di(hydrogenated tallow)dimethyl ammonium methylsulphate and di-ester variations of di(hydrogenated tallow)dimethyl ammonium chloride. Without wishing to be bound by theory, it is believed that the ester moiety(ies) lends biodegradability to these compounds. Commercially available materials are available from Witco Chemical Company Inc. of Dublin, Ohio, under the tradename "Rewoquat V3512". Details of analytical and testing procedures are given in WO95/11343, published on 27<sup>th</sup> April, 1995.

Examples of polyhydroxy compounds useful in the present invention include polyoxyethylene glycols having a weight average molecular weight of from about 200 to about 600, especially preferred is "PEG-400".

The tissue paper of the present invention may be made by common methods well-known to the person skilled in the art, such as by dewatering suitable pulp using, for example, one or more papermakers felts and/or belts.

In one embodiment of the present invention, at least one ply of the tissue paper has two primary regions. The first region comprises an imprinted region which is imprinted against the framework of the papermaking belt. The imprinted region preferably comprises an essentially continuous network. The continuous network of the first region of the paper is made on the

essentially continuous framework of the belt and will generally correspond thereto in geometry and be disposed very closely thereto in position during papermaking.

5 The second region of the paper comprises a plurality of domes dispersed throughout the imprinted network region. The domes generally correspond in geometry, and during papermaking in position, to the deflection conduits in the belt. The domes protrude outwardly from the essentially continuous network region of the paper, by conforming to the deflection conduits during the papermaking process. By conforming to the deflection conduits during the papermaking process, the fibers in the domes are deflected in the Z-direction between the paper  
10 facing surface of the framework and the paper facing surface of the reinforcing structure. Preferably the domes are discrete.

Without being bound by theory, it is believed the domes and essentially continuous network regions of the paper may have generally equivalent basis weights. By deflecting the  
15 domes into the deflection conduits, the density of the domes is decreased relative to the density of the essentially continuous network region. Moreover, the essentially continuous network region (or other pattern as may be selected) may later be imprinted as, for example, against a Yankee drying drum. Such imprinting increases the density of the essentially continuous network region relative to that of the domes.

20 The paper according to the present invention may be made according to any of commonly assigned U.S. Patents: 4,529,480, issued July 16, 1985 to Trokhan; 4,637,859, issued Jan. 20, 1987 to Trokhan; 5,364,504, issued Nov. 15, 1994 to Smurkoski et al.; and 5,529,664, issued June 25, 1996 to Trokhan et al. and 5,679,222 issued Oct. 21, 1997 to Rasch et al., the disclosures  
25 of which are incorporated herein by reference.

If desired, the paper may be dried and made on a through-air drying belt not having a patterned framework. Such paper will have discrete, high density regions and an essentially continuous low density network. During or after drying, the paper may be subjected to a differential vacuum to increase its caliper and dedensify selected regions. Such paper, and the  
30 associated belt, may be made according to the following patents: 3,301,746, issued Jan. 31, 1967 to Sanford et al.; 3,905,863, issued Sept. 16, 1975 to Ayers; 3,974,025, issued Aug. 10, 1976 to Ayers; 4,191,609, issued March 4, 1980 to Trokhan; 4,239,065, issued Dec. 16, 1980 to Trokhan;

5,366,785 issued Nov. 22, 1994 to Sawdai; and 5,520,778, issued May 28, 1996 to Sawdai, the disclosures of which are incorporated herein by reference.

In yet another embodiment, the reinforcing structure may be a felt, also referred to as a  
5 press felt as is used in conventional papermaking without through-air drying. The framework  
may be applied to the felt reinforcing structure as taught by commonly assigned U.S. Patents  
5,549,790, issued Aug. 27, 1996 to Phan; 5,556,509, issued Sept. 17, 1996 to Trokhan et al.;  
5,580,423, issued Dec. 3, 1996 to Ampulski et al.; 5,609,725, issued Mar. 11, 1997 to Phan;  
5,629,052 issued May 13, 1997 to Trokhan et al.; 5,637,194, issued June 10, 1997 to Ampulski et  
10 al.; 5,674,663, issued Oct. 7, 1997 to McFarland et al.; 5,693,187 issued Dec. 2, 1997 to  
Ampulski et al.; 5,709,775 issued Jan. 20, 1998 to Trokhan et al., 5,814,190 issued Sept. 29, 1998  
to Van Phan; and 5,817,377 issued October 6, 1998 to Trokhan et al. the disclosures of which are  
incorporated herein by reference.

15 If desired, in place of a belt having the patterned framework described above, a belt  
having a jacquard weave may be utilized. Such a belt may be utilized as a forming wire, drying  
fabric, imprinting fabric, transfer clothing etc. A jacquard weave is reported in the literature to be  
particularly useful where one does not wish to compress or imprint the paper in a nip, such as  
typically occurs upon transfer to a Yankee drying drum. Illustrative belts having a jacquard  
20 weave are found in U.S. Pat. Nos. 5,429,686 issued July 4, 1995 to Chiu et al. and 5,672,248  
issued Sept. 30, 1997 to Wendt et al.

Two or more plies of tissue paper are combined to form the multi-ply tissue. The plies  
may, optionally, be attached together by means, for example, of gluing or embossing. Gluing is  
25 less preferred because it tends to result in a stiffer, less soft product. Indeed it is preferred that no  
glue is used to attach the plies. Embossing may be used to attach the plies together, for example,  
as disclosed in EP-A-0 755 212, published on 29<sup>th</sup> January 1997. According to the present  
invention the tissue has an unembossed wiping surface over a major part of the surface area of  
the tissue. As used herein, this means that the tissue has one or more unembossed regions and,  
30 optionally, one or more embossed regions, and that the unembossed region is at least 50%, and as  
much as 100%, of the surface area of the tissue. As used herein an embossed region is a region of  
the tissue having a plurality of embossed points. Most commonly the embossed regions lie close  
to the edge of the tissue (for example along two or four edges); and embossed regions may also

be used for decorative purposes (for example to create a pattern or to spell out a logo or brand name). The unembossed region is the continuous region between and/or around the embossed regions.

5           One or both surfaces of the tissue may, optionally, be further treated with a lotion. The lotion may comprise softening/debonding agents, emollients, immobilizing agents and mixtures thereof. Suitable softening/debonding agents include quaternary ammonium compounds, polysiloxanes, and mixtures thereof. Suitable emollients include propylene glycol, glycerine, triethylene glycol, spermaceti or other waxes, petrolatum, fatty acids, fatty alcohols and fatty  
10   alcohol ethers having from 12 to 28 carbon atoms in their fatty acid chain, and mixtures thereof. Suitable immobilizing agents include polyhydroxy fatty acid esters, polyhydroxy fatty acid amides and mixtures thereof. Other optional components include perfumes, antibacterial actives, antiviral actives, disinfectants, pharmaceutical actives, film formers, deodorants, opacifiers, astringents, solvents and the like. Particular examples of lotion components include camphor,  
15   thymol and menthol.

          “Long fibers” as defined herein are considered to be of an average fiber length of at least 2.0 mm. These long paper making fibers are typically softwood fibers, preferably Northern Softwood Kraft.

20           “Short fibers” as defined herein are considered to have an average fiber length of less than 2.0 mm, preferably from 0.2mm to 1.5mm. These short papermaking fibers are typically hardwood fibers, preferably Eucalyptus fibers. Alternatively low cost sources of short fibers such as sulfite fibers, thermomechanical pulp, Chemi-ThermoMechanical Pulp (CTMP) fibers,  
25   recycled fibers, and mixtures thereof can also be used.

#### Test Methods

          The wet burst strength is measured using an electronic burst tester and the following test conditions. The burst tester is a Thwing-Albert Burst Tester Cat. No. 177 equipped with a 2000 g  
30   load cell. The burst tester is supplied by Thwing-Albert Instrument Company, Philadelphia, PA 19154, USA.

Take eight paper tissues and stack them in pairs of two. Using scissors, cut the samples so that they are approximately 228 mm in the machine direction and approximately 114 mm in the cross-machine direction, each two finished product units thick.

- 5 First age the samples for one to two hours by attaching the sample stack together with a small paper clip and "fan" the other end of the sample stack to separate the sheets, this allows circulation of air between them. Suspend each sample stack by a clamp in a 107°C ( $\pm 3^\circ\text{C}$ ) forced draft oven for 5 minutes ( $\pm 10$  seconds). After the heating period, remove the sample stack from the oven and cool for a minimum of three minutes before testing.

10

- Take one sample strip, holding the sample by the narrow cross direction edges, dipping the center of the sample into a pan filled with about 25mm of distilled water. Leave the sample in the water four ( $4.0 \pm 0.5$ ) seconds. Remove and drain for three ( $3.0 \pm 0.5$ ) seconds holding the sample so the water runs off in the cross direction. Proceed with the test immediately after the drain step. Place the wet sample on the lower ring of the sample holding device with the outer surface of the product facing up, so that the wet part of the sample completely covers the open surface of the sample holding ring. If wrinkles are present, discard the sample and repeat with a new sample. After the sample is properly in place on the lower ring, turn the switch that lowers the upper ring. The sample to be tested is now securely gripped in the sample holding unit. Start the burst test immediately at this point by pressing the start button. The plunger will begin to rise. At the point when the sample tears or ruptures, report the maximum reading. The plunger will automatically reverse and return to its original starting position. Repeat this procedure on three more samples for a total of four tests, i.e., 4 replicates. Report the results, as an average of the four replicates, to the nearest gram.

25

Caliper of the multi-ply tissue paper, as used herein, is the thickness of the paper when subjected to a compressive load of 14.7 g/m<sup>2</sup>. Preferably, caliper is measured using a low load Thwing-Albert micrometer, Model 89-11, available from the Thwing-Albert Instrument Company of Philadelphia, Pa.

30

#### Example

An aqueous slurry comprising 3% by weight of Northern Softwood Kraft (NSK) fibers was prepared in a conventional re-pulper. The NSK slurry was refined gently and a 2% solution

of the permanent wet strength resin (Kymene™ 557H) was added to the NSK stock pipe at a rate of 1% by weight of the dry fibers. The absorption of the permanent wet strength resin onto the NSK fibers is enhanced by an in-line mixer. A 1% solution of the dry strength resin (carboxymethyl cellulose) is added to the NSK stock before the fan pump at a rate of 0.15% by weight of the dry fibers. The NSK slurry was diluted to about 0.2% consistency at the fan pump.

A chemical softening composition was prepared comprising di-hard tallow diethyl ester dimethyl quaternary ammonium chloride and polyoxyethylene glycol, having an average molecular weight of 400 (PEG-400). The PEG-400 was heated to about 66°C, and the quat was dissolved into the molten PEG-400 so that a homogeneous mixture was formed.

An aqueous slurry comprising 3% by weight of eucalyptus fibers was prepared in a conventional re-pulper. A 1% solution of the chemical softening composition was added to the Eucalyptus stock pipe at a rate of 0.15% by weight of the dry fibers. The Eucalyptus slurry was diluted to about 0.2% consistency at the fan pump.

The two slurries were combined so that the ratio of NSK to eucalyptus fibers was 70:30 and the resulting slurry was deposited, by means of a single layer headbox onto a Fourdrinier wire to form an embryonic web. Dewatering occurred through the Fourdrinier wire and was assisted by a deflector and vacuum boxes. The Fourdrinier wire was a 5-shed, satin weave configuration having 3.3 machine-direction and 3.0 cross-machine direction monofilaments per millimeter respectively.

The embryonic web was transferred from the Fourdrinier wire, at a fiber consistency of about 20% at the point of transfer, to a photo-polymer fabric having 0.87 Linear Idaho cells per square millimeter (562 cells per square inch), 40% knuckle area, and 0.2 mm of photo-polymer depth. Further dewatering was accomplished by vacuum assisted drainage until the web has a fiber consistency of about 28%. The patterned web is predried by air blow-through to a fiber consistency of about 65% by weight. The web was then adhered to the surface of a Yankee dryer with a sprayed creping adhesive comprising 0.25% aqueous solution of Polyvinyl Alcohol (PVA). The fiber consistency was increased to an estimated 96% before dry creping the web with a doctor blade. The doctor blade had a bevel angle of about 25° and is positioned with respect to

the Yankee dryer to provide an impact angle of about 81°. The Yankee dryer was operated at about 4 m/s and the dried paper was formed into a roll at a reel.

5 The dry web comprised Kymene™ at a level of 0.7%, carboxymethyl cellulose at a level of 0.11%, chemical softening composition at a level of 0.05%, all by weight of dry fiber.

The web is converted into a two ply tissue paper product, having overall dimension of 210 mm square. The tissue paper product was folded and packaged without embossing.

10 In a second example the same two-ply tissue paper product was subjected to an embossing step before folding. The margin of the tissue paper product, extending about 15mm in from the edge was embossed following the process described in WO95/27429, published on 19<sup>th</sup> October 1995. The major part of the surface area of the tissue paper product (i.e. all of the surface area within the 15mm margin) was unembossed.

15 In a third example the product of the previous example was taken and decorated by embossing the brand name over a small area of the previously unembossed area. Alternatively four decorative leaf patterns were embossed in the previously unembossed area. Each decorative pattern being about 30mm square.

20 The process of the previous examples was repeated and the paper was calandared either at the reel; or during combining of the plies; or during converting; or calandared two or three times by combination of these steps.

25 The two-ply tissue paper product of these examples has a caliper of 0.45mm, an average basis weight of 50g/m<sup>2</sup> and a wet burst strength of 250 g.

30 All documents cited in the Detailed Description of the Invention are, in relevant part, incorporated herein by reference; the citation of any document is not to be construed as an admission that it is prior art with respect to the present invention.

While particular embodiments of the present invention have been illustrated and described, it would be obvious to those skilled in the art that various other changes and

modifications can be made without departing from the spirit and scope of the invention. It is therefore intended to cover in the appended claims all such changes and modifications that are within the scope of this invention.